

Contents

Volume 1

Foreword *XV*

Preface to the Fourth Edition *XVII*

1 Introduction *1*

- 1.1 Historical Perspective *1*
- 1.2 Types of Ion Chromatography *4*
- 1.3 The Ion Chromatographic System *5*
- 1.4 Advantages of Ion Chromatography *8*
- 1.5 Selection of Separation and Detection Systems *10*
- References *12*

2 Theory of Chromatography *15*

- 2.1 Chromatographic Terms *15*
- 2.1.1 Asymmetry Factor A_s *15*
- 2.2 Parameters for Assessing the Quality of a Separation *17*
- 2.2.1 Resolution *17*
- 2.2.2 Selectivity *18*
- 2.2.3 Capacity Factor *18*
- 2.3 Column Efficiency *19*
- 2.4 The Concept of Theoretical Plates (van Deemter Theory) *21*
- 2.5 van Deemter Curves in Ion Chromatography *25*
- References *27*

3 Anion-Exchange Chromatography (HPIC) *29*

- 3.1 General Remarks *29*
- 3.2 The Ion-Exchange Process *30*
- 3.3 Thermodynamic Aspects *31*
- 3.4 Stationary Phases *36*
- 3.4.1 Polymer-Based Anion Exchangers *37*

- 3.4.1.1 Poly(styrene-*co*-divinylbenzene)-Based Polymers 37
- 3.4.1.2 Polymethacrylate Resins 54
- 3.4.1.3 Polyvinylalcohol Resins 60
- 3.4.1.4 Nanobead-Agglomerated Anion Exchangers 63
- 3.4.1.5 Hyperbranched Condensation Polymers 95
- 3.4.1.6 Polymeric Monolithic Anion Exchangers 119
- 3.4.2 Silica-Based Anion Exchangers 126
- 3.4.3 Other Materials for Anion Separations 130
 - 3.4.3.1 Crown Ether and Cryptand Phases 130
 - 3.4.3.2 Alumina Phases 138
- 3.5 Eluents for Anion-Exchange Chromatography 142
- 3.6 Suppressor Systems in Anion-Exchange Chromatography 152
 - 3.6.1 Suppressor Columns 153
 - 3.6.2 Hollow Fiber Suppressors 158
 - 3.6.3 Micromembrane Suppressors 161
 - 3.6.4 Self-Regenerating Suppressors 167
 - 3.6.5 Suppressors with Monolithic Suppression Beds 172
 - 3.6.6 Capillary Suppressors 173
- 3.7 Anion-Exchange Chromatography of Inorganic Anions 175
 - 3.7.1 Overview 175
 - 3.7.2 General Parameters Affecting Retention 176
 - 3.7.3 Experimental Parameters Affecting Retention when Applying Suppressor Systems 177
 - 3.7.3.1 Choice of Eluent 177
 - 3.7.3.2 Eluent Concentration and pH Value 193
 - 3.7.3.3 Influence of Organic Solvents 198
 - 3.7.4 Experimental Parameters Affecting Retention when Applying Nonsuppressed Conductivity Detection 201
 - 3.7.4.1 Choice of Eluent 201
 - 3.7.4.2 System Peaks 210
 - 3.7.4.3 Eluent Concentration and pH Value 213
 - 3.7.5 Polarizable Anions 216
- 3.8 Anion-Exchange Chromatography of Organic Anions 227
 - 3.8.1 Carboxylic Acids 228
 - 3.8.2 Organophosphates, Organosulfates, and Organosulfonates 244
 - 3.8.3 Phosphonic and Phosphinic Acids 254
- 3.9 Gradient Elution Techniques in Anion-Exchange Chromatography of Inorganic and Organic Anions 267
 - 3.9.1 Theoretical Aspects 268
 - 3.9.2 Choice of Eluent 270
 - 3.9.3 Possibilities for Optimizing Concentration Gradients 277
 - 3.9.4 Isoconductive Techniques 278
- 3.10 Carbohydrates 281
 - 3.10.1 Sugar Alcohols 287
 - 3.10.2 Monosaccharides 290

- 3.10.3 Oligosaccharides 308
- 3.10.4 Polysaccharides 314
- 3.10.5 Carbohydrates Derived from Glycoproteins 320
 - 3.10.5.1 Compositional and Structural Analysis 323
 - 3.10.5.2 Chosen Examples 338
- 3.11 Amino Acids 341
- 3.12 Anion-Exchange Chromatography of Proteins 351
 - 3.12.1 Grafted Anion-Exchange Resins 351
 - 3.12.2 Monolithic Anion-Exchange Media 359
- 3.13 Nucleic Acids 368
- References 390

- 4 Cation-Exchange Chromatography (HPIC) 401**
 - 4.1 Stationary Phases 401
 - 4.1.1 Polymer-Based Cation Exchangers 401
 - 4.1.1.1 Poly(styrene-*co*-divinylbenzene)-Based Polymers 401
 - 4.1.1.2 Grafted Ethylvinylbenzene/Divinylbenzene Copolymers 404
 - 4.1.1.3 Polymethacrylate and Poly(vinylalcohol) Resins 432
 - 4.1.1.4 Nanobead-Agglomerated Cation Exchangers 434
 - 4.1.2 Silica-Based Cation Exchangers 439
 - 4.2 Eluents in Cation-Exchange Chromatography 448
 - 4.3 Suppressor Systems in Cation-Exchange Chromatography 450
 - 4.3.1 Suppressor Columns 450
 - 4.3.2 Hollow Fiber Suppressors 451
 - 4.3.3 Micromembrane Suppressors 451
 - 4.3.4 Self-Regenerating Suppressors 452
 - 4.3.5 Suppressors with Monolithic Suppression Beds 457
 - 4.3.6 Capillary Suppressors 458
 - 4.4 Cation-Exchange Chromatography of Alkali Metals, Alkaline-Earth Metals, and Amines 460
 - 4.5 Transition Metal Analysis 468
 - 4.5.1 Basic Theory 468
 - 4.5.2 Transition Metal Analysis by Nonsuppressed Conductivity Detection 472
 - 4.5.3 Transition Metal Analysis with Spectrophotometric Detection 474
 - 4.5.4 Chelation Ion Chromatography 490
 - 4.6 Analysis of Polyamines 496
 - 4.7 Gradient Techniques in Cation-Exchange Chromatography of Inorganic and Organic Cations 498
 - 4.8 Cation-Exchange Chromatography of Proteins 505
 - 4.8.1 Grafted Cation-Exchange Resins 507
 - 4.8.2 Monolithic Cation-Exchange Media 523
 - References 529

Volume 2

- 5 Ion-Exclusion Chromatography (HPICE) 533**
 - 5.1 The Ion-Exclusion Process 533
 - 5.2 Stationary Phases 535
 - 5.3 Eluents for Ion-Exclusion Chromatography 542
 - 5.4 Suppressor Systems in Ion-Exclusion Chromatography 543
 - 5.5 Analysis of Inorganic Acids 545
 - 5.6 Analysis of Organic Acids 550
 - 5.7 HPICE/HPIC-Coupling 553
 - 5.8 Analysis of Alcohols and Aldehydes 558
 - 5.9 Amino Acids Analysis 561
 - 5.9.1 Separation of Amino Acids 562
 - 5.9.2 Postcolumn Derivatizations of Amino Acids 570
 - 5.9.3 Sample Preparation 572
 - 5.10 Size-Exclusion Chromatography of Proteins 573
 - References 580

- 6 Ion-Pair Chromatography (MPIC) 583**
 - 6.1 Survey of Existing Retention Models 584
 - 6.2 Suppressor Systems in Ion-Pair Chromatography 588
 - 6.3 Experimental Parameters that Affect Retention 589
 - 6.3.1 Type and Concentration of Lipophilic Counterions in the Mobile Phase 590
 - 6.3.2 Type and Concentration of the Organic Modifier 593
 - 6.3.3 Inorganic Additives 596
 - 6.3.4 pH Effects and Temperature Influence 597
 - 6.4 Analysis of Surface-Inactive Ions 599
 - 6.5 Analysis of Surface-Active Ions 615
 - 6.6 Applications of the Ion-Suppression Technique 636
 - 6.7 Applications of Ion Chromatography on Mixed-Mode Stationary Phases 640
 - 6.7.1 Polymer-Based Mixed-Mode Columns 641
 - 6.7.2 Silica-Based Mixed-Mode Columns 657
 - References 679

- 7 Hydrophilic Interaction Liquid Chromatography (HILIC) 683**
 - 7.1 Separation Mechanism in Hydrophilic Interaction Liquid Chromatography 685
 - 7.2 Stationary Phases for HILIC 686
 - 7.2.1 Underivatized Silica 687
 - 7.2.2 Neutral Bonded Phases 690
 - 7.2.3 Charged Bonded Phases 696
 - 7.2.4 Zwitterionic Bonded Phases 698
 - 7.2.5 Mixed-Mode Bonded Phases 701

- 7.3 Factors Affecting Retention in HILIC 707
 - 7.3.1 Organic Solvents 707
 - 7.3.2 Ionic Additives 708
 - 7.3.3 Mobile-Phase pH 709
- 7.4 Applications 710
 - 7.4.1 Carbohydrates and Amino Acids 710
 - 7.4.2 Organic Acids 713
 - 7.4.3 Hydrophilic Active Pharmaceutical Ingredients 718
 - 7.4.4 Buffer Salts for Biopharmaceutical Applications 720
 - 7.4.5 Nucleobases, Nucleosides, and Nucleotides 721
 - 7.4.6 Melamine and Cyanuric Acid 725
- References 728

- 8 Detection Methods in Ion Chromatography 731**
 - 8.1 Electrochemical Detection Methods 731
 - 8.1.1 Conductivity Detection 731
 - 8.1.1.1 Theoretical Principles 732
 - 8.1.1.2 Application Modes of Conductivity Detection 738
 - 8.1.2 Amperometric Detection 743
 - 8.1.2.1 Fundamental Principles of Voltammetry 744
 - 8.1.2.2 Amperometry 748
 - 8.1.3 Charge Detection 771
 - 8.1.3.1 The Charge Signal 774
 - 8.1.3.2 Calibration Behavior in Charge Detection 776
 - 8.1.3.3 Example Applications 778
 - 8.2 Spectrometric Detection Methods 782
 - 8.2.1 UV/Vis Detection 782
 - 8.2.1.1 Direct UV/Vis Detection 782
 - 8.2.1.2 UV/Vis Detection in Combination with Derivatization Techniques 783
 - 8.2.1.3 Indirect UV Detection 799
 - 8.2.2 Fluorescence Detection 803
 - 8.3 Aerosol-Based Detection Methods 810
 - 8.3.1 Evaporative Light Scattering Detection 811
 - 8.3.1.1 Advantages and Limitations of ELSD 814
 - 8.3.1.2 Applications of ELSD 816
 - 8.3.2 Condensation Nucleation Light Scattering Detection 819
 - 8.3.3 Charged Aerosol Detection 822
 - 8.3.3.1 Applications of CAD 829
 - 8.4 Other Detection Methods 844
 - 8.4.1 Refractive Index Detection 844
 - 8.4.2 Radioactivity Monitoring 847
 - 8.4.3 Chemiluminescence Detection 848
 - 8.5 Hyphenated Techniques 853
 - 8.5.1 IC-ICP Coupling 853
 - 8.5.2 IC-MS Coupling 865

- 8.5.2.1 Electrospray Interface 867
- 8.5.2.2 IC-MS Applications 875
- References 926

- 9 Quantitative Analysis 935**
- 9.1 General 935
- 9.2 Analytical Chemical Information Parameters 936
- 9.3 Determination of Peak Areas 937
- 9.3.1 Manual Determination of Peak Areas and Peak Heights 938
- 9.3.2 Electronic Peak Area Determination 940
- 9.4 Statistical Quantities 944
- 9.4.1 Mean Value 944
- 9.4.2 Standard Deviation 945
- 9.4.3 Scatter and Confidence Interval 945
- 9.5 Calibration of an Analytical Method (Basic Calibration) 946
- 9.5.1 Acquisition of the Calibration Function 947
- 9.5.1.1 Method Characteristic Parameters of a Linear Calibration Function 948
- 9.5.1.2 Method Parameters of a Calibration Function of Second Degree 950
- 9.5.2 Testing of the Basic Calibration 952
- 9.5.3 Testing the Precision 953
- 9.5.3.1 Homogeneity of Variances 953
- 9.5.3.2 Outlier Tests 953
- 9.5.4 Calibration Methods 955
- 9.5.4.1 Area Normalization 955
- 9.5.4.2 Internal Standard 956
- 9.5.4.3 External Standard 957
- 9.5.4.4 Standard Addition 958
- 9.6 Detection Criteria, Limit of Detection, Limit of Determination 960
- 9.6.1 Determination of Detection Criteria, Limit of Detection, and Limit of Determination 961
- 9.7 The System of Quality Control Cards 964
- 9.7.1 Types of Quality Control Cards and Their Applications 965
- References 972

Volume 3

- 10 Applications 975**
- 10.1 Ion Chromatography in Environmental Analysis 977
- 10.1.1 Conventional Water Analysis 977
- 10.1.2 Analysis of Water Disinfection By-Products 996
- 10.1.2.1 Analysis of Bromate and Other Oxyhalides 997
- 10.1.2.2 Analysis of Haloacetic Acids 1021

- 10.1.3 Perchlorate Analysis 1024
- 10.1.4 Analysis of Highly Contaminated Water Samples 1038
 - 10.1.4.1 Seawater Analysis 1041
 - 10.1.4.2 Soil Analysis 1048
 - 10.1.4.3 Air Analysis 1053
- 10.1.5 Other Environmental Applications 1066
- 10.2 Ion Chromatography in Power Plant Chemistry 1068
 - 10.2.1 High-Purity Water Analysis 1069
 - 10.2.1.1 Conventional Preconcentration Techniques 1070
 - 10.2.1.2 Large-Volume Direct Injection Techniques 1077
 - 10.2.1.3 RFIC-ESP 1081
 - 10.2.1.4 Capillary Ion Chromatography 1084
 - 10.2.2 Analysis of Conditioned Waters 1085
 - 10.2.3 Cooling Water Analysis 1094
 - 10.2.4 Flue Gas Scrubber Solutions 1106
 - 10.2.5 Analysis of Chemicals 1111
- 10.3 Ion Chromatography in the Semiconductor Industry 1114
 - 10.3.1 High-Purity Water Analysis 1115
 - 10.3.2 Surface Contaminations 1123
 - 10.3.3 Solvents 1128
 - 10.3.4 Acids, Bases, and Etching Agents 1132
 - 10.3.4.1 Solar Cell Manufacturing 1142
 - 10.3.5 Other Applications 1143
- 10.4 Ion Chromatography in the Electroplating Industry 1148
 - 10.4.1 Analysis of Inorganic Anions 1149
 - 10.4.2 Analysis of Metal Complexes 1157
 - 10.4.3 Analysis of Organic Acids 1159
 - 10.4.4 Analysis of Inorganic Cations 1161
 - 10.4.5 Analysis of Organic Additives 1162
- 10.5 Ion Chromatography in the Detergent and Household Product Industry 1175
 - 10.5.1 Detergents 1175
 - 10.5.2 Household Products 1184
- 10.6 Ion Chromatography in the Food and Beverage Industry 1194
 - 10.6.1 Beverages 1197
 - 10.6.2 Dairy Products 1224
 - 10.6.3 Meat Processing 1233
 - 10.6.4 Baby Food 1237
 - 10.6.5 Groceries and Luxuries 1254
 - 10.6.6 Sweeteners 1264
- 10.7 Ion Chromatography in the Pharmaceutical Industry 1271
 - 10.7.1 Counterion Analysis 1272
 - 10.7.2 Analysis of Amines 1283
 - 10.7.3 Analysis of Organic Acids 1291
 - 10.7.4 Antibiotics 1295

10.7.5	Ionic Drugs	1311
10.7.6	Assays for Active Pharmaceutical Ingredients and Counterions	1315
10.7.7	Other Pharmaceutical Applications	1318
10.7.8	Biotechnology Applications	1325
10.8	Ion Chromatography in Clinical Chemistry	1336
10.9	Oligosaccharide Analysis of Membrane-Coupled Glycoproteins	1361
10.10	Chemical and Petrochemical Applications	1367
10.10.1	Chemical Applications	1367
10.10.2	Petrochemical Applications	1393
10.10.2.1	Combustion Ion Chromatography	1407
10.10.2.2	Biofuel Applications	1409
10.11	Other Applications	1417
10.12	Sample Preparation and Matrix Problems	1423
10.12.1	Sample Filtration and Preservation	1425
10.12.2	Sample Dilution	1431
10.12.3	Sample Pretreatment Cartridges	1437
10.12.4	Sample Neutralization	1443
10.12.5	Combustion Techniques	1446
10.12.6	Dialysis Techniques	1453
10.12.7	Chemical Modifications of Samples	1455
10.13	Concluding Remarks	1459
	References	1461
	Index	1485